

(19) World Intellectual Property  
Organization  
International Bureau



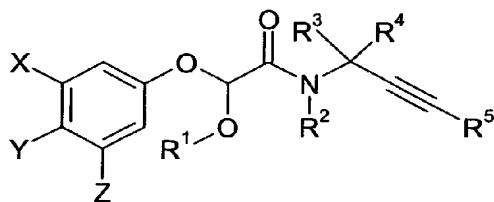
(43) International Publication Date  
24 June 2004 (24.06.2004)

PCT

(10) International Publication Number  
**WO 2004/052100 A1**

- (51) International Patent Classification<sup>7</sup>: **A01N 39/04**,  
C07C 235/20, 235/22
- (21) International Application Number:  
PCT/GB2003/004612
- (22) International Filing Date: 27 October 2003 (27.10.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0227557.6 26 November 2002 (26.11.2002) GB
- (71) Applicant (for all designated States except US): **SYNGENTA LIMITED** [GB/GB]; European Regional Centre, Priestley Road, Surrey Research Park, Guildford, Surrey GU2 7YH (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **CROWLEY, Patrick, Jelf** [GB/GB]; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell, Berks RG42 6EY (GB). **SALMON, Roger** [GB/GB]; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell, Berks RG42 6EY (GB).
- (74) Agents: **HOUGHTON, Malcolm, John et al.**; Intellectual Property Department, Syngenta Limited, P.O. Box 3538, Jealott's Hill International Research Centre, Bracknell, Berks RG42 6YA (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FUNGICIDES



(1)

(57) Abstract: The use as a plant fungicide of a compound of general formula (1). Also included are plant fungicidal compositions containing these compounds and some of the compounds themselves.

WO 2004/052100 A1

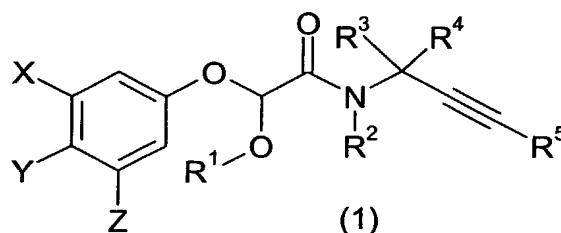
# FUNGICIDES

This invention relates to the use as plant fungicides of certain *N*-alkynyl-2-alkoxy-2-(substituted phenoxy)alkylamides. It also relates to plant fungicidal compositions  
 5 containing these compounds and to some of the compounds themselves.

Certain *N*-alkynyl-2-(substituted phenoxy)alkylamides are described in US 4,116,677 as being useful as herbicides. Others are described in US 4,168,319 as being useful as mildewicides. Several *N*-dimethylpropynyl- $\alpha$ -methoxy- and  $\alpha$ -ethoxy- $\alpha$ -(substituted phenoxy)acetamides are described in US 4,062,977 for use as miticides and  
 10 the compound *N*-dimethylpropynyl- $\alpha$ -methoxy- $\alpha$ -(3,5-dimethylphenoxy)acetamide is described in US 4,083,867 for use as a herbicide.

The present invention is concerned with the provision of particular *N*-alkynyl-2-alkoxy-2-(substituted phenoxy)alkylamides for use as plant fungicides.

Thus according to the present invention there is provided the use as a plant  
 15 fungicide of a compound of the general formula (1):



wherein

X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl (e.g. methyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub>  
 20 alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxy carbonyl,  
 25 -CONR'R'', -COR', -NR'COR'' or -NR'COOR''' where R' and R'' are independently H or C<sub>1-4</sub> alkyl and R''' is C<sub>1-4</sub> alkyl (e.g. acetyl, -NHCOCH<sub>3</sub> and -NHCO<sub>2</sub>CH<sub>3</sub>), provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (i.e. methyl, ethyl, *n*-propyl or *n*-butyl);

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does

5 not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally  
10 substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

15 R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub>  
20 alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl,  
25 halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

The compounds of the invention contain at least one asymmetric carbon atom (and at least two when R<sup>3</sup> and R<sup>4</sup> are different) and may exist as enantiomers (or as pairs  
30 of diastereoisomers) or as mixtures of such. However, these mixtures may be separated into individual isomers or isomer pairs, and this invention embraces such isomers and

mixtures thereof in all proportions. It is to be expected that for any given compound, one isomer may be more fungicidally active than another.

Except where otherwise stated, alkyl groups and alkyl moieties of alkoxy, alkylthio, etc., suitably contain from 1 to 4 carbon atoms in the form of straight or  
5 branched chains. Examples are methyl, ethyl, *n*- and *iso*-propyl and *n*-, *sec*-, *iso*- and *tert*-butyl. Where alkyl moieties contain 5 or 6 carbon atoms, examples are *n*-pentyl and *n*-hexyl.

Alkenyl and alkynyl moieties also suitable contain from 2 to 4 carbon atoms in the form of straight or branched chains. Examples are allyl, ethynyl and propargyl.

10 Halo includes fluoro, chloro, bromo and iodo. Most commonly it is fluoro, chloro or bromo and usually fluoro or chloro.

The substituents X, Y and Z on the phenyl ring of formula (1) may provide a 3-, 3, 5- or 3, 4, 5- substituted phenyl ring. Typically X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or  
15 methoxy and Y is H, chloro, bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and both Y and Z are H.

$R^1$  is methyl, ethyl, *n*-propyl or *n*-butyl. Methyl and ethyl are preferred values of  $R^1$ .

20 Typically  $R^2$  is H and at least one, but preferably both of  $R^3$  and  $R^4$  are methyl. When one of  $R^3$  and  $R^4$  is H, the other may be methyl, ethyl or *n*- or *iso*-propyl. When one of  $R^3$  and  $R^4$  is methyl, the other may be H or ethyl but is preferably also methyl.  $R^2$  also includes  $C_{1-4}$  alkoxymethyl and benzyloxymethyl in which the phenyl ring of the benzyl group optionally carries an alkoxy substituent, e.g. a methoxy substituent. Such  
25 values of  $R^2$  provide compounds of formula (1) that are believed to be pro-pesticidal compounds.

Typically  $R^5$  is H, methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxymethyl, 3-cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthio-propyl, 3-methanesulphinylpropyl or 3-methanesulphonylpropyl. Of particular interest are  
30 compounds where  $R^5$  is methyl, methoxymethyl or 3-cyanopropyl.

In one aspect, the invention provides the use as a plant fungicide of a compound of the general formula (1) wherein

- X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl (e.g. methyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R", -COR' or -NR'COR" where R' and R" are independently H or C<sub>1-4</sub> alkyl (e.g. -NHCOCH<sub>3</sub>), provided that at least one of X and Z is other than H;
- R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (i.e. methyl, ethyl, *n*-propyl or *n*-butyl);
- 10 R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;
- R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or
- 15 R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and
- R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, C<sub>1-6</sub> alkylthio, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy or mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or
- 20 R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,
- 25 in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl,
- 30

halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

In another aspect, the invention provides the use as a plant fungicide of a  
5 compound of the general formula (1) wherein X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or methoxy and Y is H, chloro, bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and both Y and Z are H; R<sup>1</sup> is methyl, ethyl, *n*-propyl or *n*-butyl; R<sup>2</sup> is H; R<sup>3</sup> and R<sup>4</sup> are  
10 both methyl; and R<sup>5</sup> is H, methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxymethyl, 3-cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthiopropyl, 3-methanesulphinylpropyl or 3-methanesulphonylpropyl. Preferably R<sup>1</sup> is methyl or ethyl. Preferably R<sup>5</sup> is methyl, methoxymethyl or 3-cyanopropyl.

The invention also includes those compounds of the general formula (1) that are  
15 novel. Thus in another aspect the invention provides a compound of the general formula (1) wherein

X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl (e.g. methyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where  
20 *n* is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R'', -COR', -NR'COR'' or -NR'COOR''' where R' and R'' are independently H or C<sub>1-4</sub> alkyl and R''' is C<sub>1-4</sub> alkyl (e.g. acetyl, -NHCOCH<sub>3</sub> and -NHCO<sub>2</sub>CH<sub>3</sub>), provided that  
25 at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (i.e. methyl, ethyl, *n*-propyl or *n*-butyl);

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both  
30 are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4

membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy,

- 5 aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

- R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted  
10 benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio,

- 15 hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub>  
20 cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy;

- provided that R<sup>5</sup> is not H when (i) X, Z, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and Y, and R<sup>2</sup> are both H, (ii) X, Z, R<sup>3</sup> and R<sup>4</sup> are all methyl, Y is chloro, R<sup>1</sup> is ethyl and R<sup>2</sup> is H, (iii) X and Z are both chloro, R<sup>1</sup> is methyl or ethyl, R<sup>3</sup> and R<sup>4</sup> are both methyl and Y and R<sup>2</sup> are both  
25 H, (iv) X, Y and Z are all chloro, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and R<sup>2</sup> is H, and (v) Y is chloro, Z is trifluoromethyl, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and X and R<sup>2</sup> are both H.

In yet another aspect the invention provides a compound of the general formula (1) wherein

- X, Y and Z are independently H, fluoro, bromo, iodo, C<sub>2-4</sub> alkyl (e.g. ethyl), halo(C<sub>1-4</sub>)-  
30 alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)-alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>-(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro

(e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R", -COR', -NR'COR" or -NR'COOR"" where R' and R" are independently H or C<sub>1-4</sub> alkyl and R"" is C<sub>1-4</sub> alkyl (e.g. acetyl, -NHCOCH<sub>3</sub> and

5 -NHCO<sub>2</sub>CH<sub>3</sub>), provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (i.e. methyl, ethyl, *n*-propyl or *n*-butyl);

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both  
10 are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

15 R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally  
20 substituted thienylmethoxy, or

R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy,

25 mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>,  
30 -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub>



cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

In yet another aspect the invention provides a compound of the general formula (1) wherein

- 5 X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl (e.g. methyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted
  - 10 with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R", -COR', -NR'COR" or -NR'COOR"" where R' and R" are independently H or C<sub>1-4</sub> alkyl and R"" is C<sub>1-4</sub> alkyl (e.g. acetyl, -NHCOCH<sub>3</sub> and -NHCO<sub>2</sub>CH<sub>3</sub>), provided that at least one of X and Z is other than H;
  - R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (i.e. methyl, ethyl, *n*-propyl or *n*-butyl);
  - 15 R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;
  - R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or
  - 20 R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and
  - R<sup>5</sup> is C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy,
  - 25 aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or
  - R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted
  - 30 benzyl,
- in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy,

mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro,  
 5 -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>,  
 -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

10 In yet another aspect the invention provides a compound of the general formula (1) wherein  
 X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl (e.g. methyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where  
 15 n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxy-carbonyl, -CONR'R", -COR' or -NR'COR" where R' and R" are independently H or C<sub>1-4</sub> alkyl (e.g. -NHCOCH<sub>3</sub>), provided that at least one of X and Z is other than H;  
 20 R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (e.g. methyl, ethyl, *n*-propyl or *n*-butyl);  
 R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;  
 R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does  
 25 not exceed 4, or  
 R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and  
 R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally  
 30 substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, C<sub>1-6</sub> alkylthio, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy or mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, tri(C<sub>1-4</sub>)alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted

benzyloxy or optionally substituted thienylmethoxy, or

R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are

5 optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro,  
10 -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy;

15 provided that R<sup>5</sup> is not H when (i) X, Z, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and Y, and R<sup>2</sup> are both H, (ii) X, Z, R<sup>3</sup> and R<sup>4</sup> are all methyl, Y is chloro, R<sup>1</sup> is ethyl and R<sup>2</sup> is H, (iii) X and Z are both chloro, R<sup>1</sup> is methyl or ethyl, R<sup>3</sup> and R<sup>4</sup> are both methyl and Y and R<sup>2</sup> are both H, (iv) X, Y and Z are all chloro, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and R<sup>2</sup> is H, and (v) Y is chloro, Z is trifluoromethyl, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and X and R<sup>2</sup> are both H.

20 In yet another aspect the invention provides a compound of the general formula (1) wherein

X, Y and Z are independently H, fluoro, bromo, iodo, C<sub>2-4</sub> alkyl (e.g. ethyl), halo(C<sub>1-4</sub>)alkyl (e.g. trifluoromethyl), C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy (e.g. methoxy), halo(C<sub>1-4</sub>)alkoxy (e.g. trifluoromethoxy), -S(O)<sub>n</sub>-(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl), -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R'', -COR' or -NR'COR'' where R' and R'' are independently H or C<sub>1-4</sub> alkyl (e.g. -NHCOCH<sub>3</sub>), provided that at least one of X and Z is other than H;  
25 R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (e.g. methyl, ethyl, *n*-propyl or *n*-butyl);  
R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

30

$R^3$  and  $R^4$  are independently H,  $C_{1-3}$  alkyl,  $C_{2-3}$  alkenyl or  $C_{2-3}$  alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

$R^3$  and  $R^4$  join with the carbon atom to which they are attached to form a 3 or 4

5 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or  $C_{1-4}$  alkyl; and

$R^5$  is H,  $C_{1-4}$  alkyl or  $C_{3-6}$  cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy,  $C_{1-6}$  alkoxy,  $C_{1-6}$  alkylthio, cyano,  $C_{1-4}$  alkylcarbonyloxy, aminocarbonyloxy or mono- or di( $C_{1-4}$ )alkylaminocarbonyloxy, tri( $C_{1-4}$ )alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

10  $R^5$  is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the  $R^5$  values are

15 optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto,  $C_{1-4}$  alkyl,  $C_{2-4}$  alkenyl,  $C_{2-4}$  alkynyl,  $C_{1-4}$  alkoxy,  $C_{2-4}$  alkenyloxy,  $C_{2-4}$  alkynyloxy, halo( $C_{1-4}$ )alkyl, halo( $C_{1-4}$ )alkoxy,  $C_{1-4}$  alkylthio, halo( $C_{1-4}$ )alkylthio, hydroxy( $C_{1-4}$ )alkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl,  $C_{3-6}$  cycloalkyl,  $C_{3-6}$  cycloalkyl( $C_{1-4}$ )alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, 20  $-NR^mR^n$ ,  $-NHCOR^m$ ,  $-NHCONR^mR^n$ ,  $-CONR^mR^n$ ,  $-SO_2R^m$ ,  $-OSO_2R^m$ ,  $-COR^m$ ,  $-CR^m=NR^n$  or  $-N=CR^mR^n$ , in which  $R^m$  and  $R^n$  are independently hydrogen,  $C_{1-4}$  alkyl, halo( $C_{1-4}$ )alkyl,  $C_{1-4}$  alkoxy, halo( $C_{1-4}$ )alkoxy,  $C_{1-4}$  alkylthio,  $C_{3-6}$  cycloalkyl,  $C_{3-6}$  cycloalkyl( $C_{1-4}$ )alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen,  $C_{1-4}$  alkyl or  $C_{1-4}$  alkoxy.

25 In yet another aspect the invention provides a compound of the general formula (1) wherein

X, Y and Z are independently H, halogen,  $C_{1-4}$  alkyl (e.g. methyl), halo( $C_{1-4}$ )alkyl (e.g. trifluoromethyl),  $C_{2-4}$  alkenyl, halo( $C_{2-4}$ )alkenyl,  $C_{2-4}$  alkynyl, halo( $C_{2-4}$ )alkynyl,  $C_{1-4}$  alkoxy (e.g. methoxy), halo( $C_{1-4}$ )alkoxy (e.g. trifluoromethoxy),  $-S(O)_n(C_{1-4})$ alkyl where 30 n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro (e.g. methylthio, trifluoromethylsulphonyl),  $-OSO_2(C_{1-4})$ alkyl where the alkyl group is optionally substituted with fluoro (e.g. trifluoromethylsulphonyloxy), cyano, nitro,  $C_{1-4}$  alkoxy-

carbonyl, -CONR'R", -COR' or -NR'COR" where R' and R" are independently H or C<sub>1-4</sub> alkyl (e.g. -NHCOCH<sub>3</sub>), provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group (e.g. methyl, ethyl, *n*-propyl or *n*-butyl);

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the

5 benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4

10 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, C<sub>1-6</sub> alkylthio, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy or mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, tri(C<sub>1-4</sub>)alkylsilyloxy,

15 optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are

20 optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)-alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)-alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro,

25 -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

30 In still yet another aspect, the invention provides a compound of the general formula (1) wherein X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or methoxy and Y is H, chloro,

bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and both Y and Z are H; R<sup>1</sup> is methyl, ethyl, *n*-propyl or *n*-butyl; R<sup>2</sup> is H; R<sup>3</sup> and R<sup>4</sup> are both methyl; and R<sup>5</sup> is methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxymethyl, 3-cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthiopropyl, 3-methanesulphinylpropyl or 3-methanesulphonylpropyl. Preferably R<sup>1</sup> is methyl or ethyl. Preferably R<sup>5</sup> is methyl, methoxymethyl or 3-cyanopropyl

Compounds that form part of the invention are illustrated in Tables 1 to 26 below.

The compounds in Table 1 are of the general formula (1) where R<sub>1</sub> is ethyl, R<sup>2</sup> is H, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methyl and X, Y and Z have the values given in the table.

**Table 1**

Compound No	X	Y	Z
1	Cl	Cl	CN
2	Cl	Cl	Cl
3	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
4	Cl	H	Cl
5	Cl	CH <sub>3</sub>	Cl
6	Br	H	Br
7	Br	CH <sub>3</sub>	Br
8	CH <sub>3</sub>	H	CH <sub>3</sub>
9	CH <sub>3</sub>	Cl	CH <sub>3</sub>
10	CH <sub>3</sub>	Br	CH <sub>3</sub>
11	CH <sub>3</sub>	CH <sub>3</sub> S	CH <sub>3</sub>
12	CH <sub>3</sub> O	H	CH <sub>3</sub> O
13	CH <sub>3</sub> O	Cl	CH <sub>3</sub> O
14	CH <sub>3</sub> O	Br	CH <sub>3</sub> O
15	CH <sub>3</sub> O	CH <sub>3</sub> S	CH <sub>3</sub> O
16	CH <sub>3</sub> O	H	CN
17	CH <sub>3</sub> O	H	Cl
18	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>

19	Cl	H	H
20	Br	H	H
21	CF <sub>3</sub>	H	H
22	Br	Cl	H
23	Br	Br	H
24	Br	F	H
25	Br	CN	H
26	Br	CF <sub>3</sub> O	H
27	Br	CH <sub>3</sub> S	H
28	Br	HC≡C-	H
29	Br	CH <sub>2</sub> =CH-	H
30	H	CH <sub>3</sub> O	H
31	Br	COCH <sub>3</sub>	H
32	Br	CF <sub>3</sub>	H
33	F	H	H
34	CN	H	H
35	CH <sub>3</sub>	H	H
36	CH <sub>3</sub> CO	H	H
37	CH <sub>3</sub> O	H	H
38	CF <sub>3</sub> O	H	H
39	CH <sub>3</sub> S	H	H
40	HC≡C-	H	H
41	H <sub>2</sub> C=CH-	H	H
42	F	H	F
43	F	H	Cl
44	F	H	Br
45	F	H	CH <sub>3</sub> O
46	F	H	CH <sub>3</sub> CO
47	F	H	CN
48	F	H	CH <sub>3</sub>
49	F	H	CF <sub>3</sub> O

50	F	H	CF <sub>3</sub>
51	F	H	CH <sub>3</sub> S
52	F	H	COOCH <sub>3</sub>
53	Cl	H	Br
54	Cl	H	CH <sub>3</sub> CO
55	Cl	H	CH <sub>3</sub>
56	Cl	H	CN
57	Cl	H	CF <sub>3</sub> O
58	Cl	H	CF <sub>3</sub>
59	Cl	H	CH <sub>3</sub> S
60	Cl	H	COOCH <sub>3</sub>
61	Cl	H	CON(CH <sub>3</sub> ) <sub>2</sub>
62	Cl	H	NHCOOCH <sub>3</sub>
63	Cl	H	OSO <sub>2</sub> CH <sub>3</sub>
64	Cl	H	HC≡C-
65	Cl	H	CH <sub>2</sub> =CH-
66	Br	H	CH <sub>3</sub>
67	Br	H	CN
68	CN	H	CN
69	CN	H	CH <sub>3</sub>
70	CN	H	CF <sub>3</sub> O
71	CF <sub>3</sub> O	H	CF <sub>3</sub> O
72	CF <sub>3</sub>	H	CF <sub>3</sub>
73	CH <sub>3</sub>	H	CH <sub>3</sub> O
74	F	F	H
75	F	Cl	H
76	F	Br	H
77	F	CH <sub>3</sub> O	H
78	F	CN	H
79	F	CH <sub>3</sub>	H
80	Cl	Cl	H



81	Cl	F	H
82	Cl	Br	H
83	Cl	CN	H
84	Cl	CH <sub>3</sub>	H
85	Cl	CH <sub>3</sub> O	H
86	Cl	CF <sub>3</sub> O	H
87	Cl	CH <sub>3</sub> S	H
88	Cl	CH <sub>3</sub> SO <sub>2</sub> O	H
89	Cl	CH <sub>3</sub> CO	H
90	CN	F	H
91	CN	Cl	H
92	CN	CH <sub>3</sub> O	H
93	CH <sub>3</sub> O	CH <sub>3</sub> O	H
94	CH <sub>3</sub> O	Cl	H
95	CH <sub>3</sub> O	CN	H
96	CH <sub>3</sub> CO	Cl	H
97	CF <sub>3</sub> O	Cl	H
98	CF <sub>3</sub> O	CN	H
99	CH <sub>3</sub> S	Cl	H
100	CH <sub>3</sub> S	F	H
101	CH <sub>3</sub> S	CH <sub>3</sub>	H
102	CH <sub>3</sub> SO <sub>2</sub> O	Cl	H
103	Cl	Cl	F
104	Cl	Cl	Br
105	Cl	Cl	CH <sub>3</sub> O
106	Cl	Cl	CH <sub>3</sub> CO
107	Cl	Cl	CH <sub>3</sub> S
108	Cl	F	Cl
109	Cl	CH <sub>3</sub> O	Cl
110	Cl	CF <sub>3</sub> O	Cl
111	Cl	CH <sub>3</sub> SO	Cl

112	Cl	CH <sub>3</sub> SO <sub>2</sub>	Cl
113	Cl	OSO <sub>2</sub> CH <sub>3</sub>	Cl
114	Cl	CH <sub>3</sub> CO	Cl
115	Cl	CO <sub>2</sub> CH <sub>3</sub>	Cl
116	Cl	CON(CH <sub>3</sub> ) <sub>2</sub>	Cl
117	Cl	HC≡C-	Cl
118	Cl	CH <sub>2</sub> =CH-	Cl
119	Cl	NHCO <sub>2</sub> CH <sub>3</sub>	Cl
120	F	F	F
121	F	F	CN
122	F	F	CH <sub>3</sub>
123	F	F	CH <sub>3</sub> O
124	F	CH <sub>3</sub> O	F
125	F	CF <sub>3</sub> O	F
126	F	CH <sub>3</sub> SO	F
127	F	CH <sub>3</sub> SO <sub>2</sub>	F
128	F	OSO <sub>2</sub> CH <sub>3</sub>	F
129	F	CH <sub>3</sub> CO	F
130	F	CO <sub>2</sub> CH <sub>3</sub>	F
131	CH <sub>3</sub> O	CH <sub>3</sub> O	CH <sub>3</sub> O
132	CH <sub>3</sub> O	CH <sub>3</sub> O	Cl
133	CH <sub>3</sub> O	CH <sub>3</sub> O	CH <sub>3</sub>
134	Cl	CN	Cl

Table 2

Table 2 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 2 is the same as compound 1 of Table 1 except that in compound 1 of Table 2 R<sup>1</sup> is methyl instead of ethyl. Similarly, compounds 2 to 134 of Table 2 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 2 R<sup>1</sup> is methyl instead of ethyl.

Table 3

Table 3 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is methyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 3 is the same as compound 1 of Table 1 except that in compound 1 of Table 3 R<sup>1</sup> is *n*-propyl instead of ethyl. Similarly, compounds 2 to 134 of Table 3 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 3 R<sup>1</sup> is *n*-propyl instead of ethyl.

Table 4

Table 4 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 4 is the same as compound 1 of Table 1 except that in compound 1 of Table 4 R<sup>1</sup> is *n*-butyl instead of ethyl. Similarly, compounds 2 to 134 of Table 4 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 4 R<sup>1</sup> is *n*-butyl instead of ethyl.

Table 5

Table 5 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is H and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 5 is the same as compound 1 of Table 1 except that in compound 1 of Table 5 R<sup>5</sup> is H instead of methyl. Similarly, compounds 2 to 134 of Table 5 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 5 R<sup>5</sup> is H instead of methyl.

Table 6

Table 6 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is H and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 6 is the same as compound 1 of Table 2 except that in compound 1 of Table 6 R<sup>5</sup> is H instead of methyl. Similarly, compounds 2 to 134 of Table 6 are the same as compounds 2 to 134 of Table 2, respectively, except that in the compounds of Table 6 R<sup>5</sup> is H instead of methyl.

Table 7

Table 7 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is H and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 7 is the same as compound 1 of Table 3 except

that in compound 1 of Table 7 R<sup>5</sup> is H instead of methyl. Similarly, compounds 2 to 134 of Table 7 are the same as compounds 2 to 134 of Table 3, respectively, except that in the compounds of Table 7 R<sup>5</sup> is H instead of methyl.

#### Table 8

5 Table 8 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is H and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 8 is the same as compound 1 of Table 4 except that in compound 1 of Table 8 R<sup>5</sup> is H instead of methyl. Similarly, compounds 2 to 134 of Table 8 are the same as compounds 2 to 134 of Table 4, respectively, except that in the  
10 compounds of Table 8 R<sup>5</sup> is H instead of methyl.

#### Table 9

Table 9 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is hydroxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 9 is the same as compound 1 of  
15 Table 1 except that in compound 1 of Table 9 R<sup>5</sup> is hydroxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 9 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 9 R<sup>5</sup> is hydroxymethyl instead of methyl.

#### Table 10

20 Table 10 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is hydroxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 10 is the same as compound 1 of Table 2 except that in compound 1 of Table 10 R<sup>5</sup> is hydroxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 10 are the same as compounds 2 to 134 of Table  
25 2, respectively, except that in the compounds of Table 10 R<sup>5</sup> is hydroxymethyl instead of methyl.

#### Table 11

Table 11 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is hydroxymethyl and X, Y and Z have  
30 the values listed in Table 1. Thus compound 1 of Table 11 is the same as compound 1 of Table 3 except that in compound 1 of Table 11 R<sup>5</sup> is hydroxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 11 are the same as compounds 2 to 134 of Table

3, respectively, except that in the compounds of Table 11 R<sup>5</sup> is hydroxymethyl instead of methyl.

#### Table 12

Table 12 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is hydroxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 12 is the same as compound 1 of Table 4 except that in compound 1 of Table 12 R<sup>5</sup> is hydroxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 12 are the same as compounds 2 to 134 of Table 4, respectively, except that in the compounds of Table 12 R<sup>5</sup> is hydroxymethyl instead of methyl.

#### Table 13

Table 13 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methoxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 13 is the same as compound 1 of Table 1 except that in compound 1 of Table 13 R<sup>5</sup> is methoxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 13 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 13 R<sup>5</sup> is methoxymethyl instead of methyl.

#### Table 14

Table 14 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methoxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 14 is the same as compound 1 of Table 2 except that in compound 1 of Table 14 R<sup>5</sup> is methoxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 14 are the same as compounds 2 to 134 of Table 2, respectively, except that in the compounds of Table 14 R<sup>5</sup> is methoxymethyl instead of methyl.

#### Table 15

Table 15 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is methoxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 15 is the same as compound 1 of Table 3 except that in compound 1 of Table 15 R<sup>5</sup> is methoxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 15 are the same as compounds 2 to 134 of Table

3, respectively, except that in the compounds of Table 15 R<sup>5</sup> is methoxymethyl instead of methyl.

#### Table 16

Table 16 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is methoxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 16 is the same as compound 1 of Table 4 except that in compound 1 of Table 16 R<sup>5</sup> is methoxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 16 are the same as compounds 2 to 134 of Table 4, respectively, except that in the compounds of Table 16 R<sup>5</sup> is methoxymethyl instead of methyl.

#### Table 17

Table 17 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 17 is the same as compound 1 of Table 1 except that in compound 1 of Table 17 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 17 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 17 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl.

#### Table 18

Table 18 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 18 is the same as compound 1 of Table 2 except that in compound 1 of Table 18 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 18 are the same as compounds 2 to 134 of Table 2, respectively, except that in the compounds of Table 18 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl.

#### Table 19

Table 19 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 19 is the same as compound 1 of Table 3 except that in compound 1 of Table 19 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table

19 are the same as compounds 2 to 134 of Table 3, respectively, except that in the compounds of Table 19 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl.

#### Table 20

Table 20 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 20 is the same as compound 1 of Table 4 except that in compound 1 of Table 20 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl. Similarly, compounds 2 to 134 of Table 20 are the same as compounds 2 to 134 of Table 4, respectively, except that in the compounds of Table 20 R<sup>5</sup> is *tert*-butyldimethylsilyloxymethyl instead of methyl.

#### Table 21

Table 21 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is 1-methoxyethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 21 is the same as compound 1 of Table 1 except that in compound 1 of Table 21 R<sup>5</sup> is 1-methoxyethyl instead of methyl. Similarly, compounds 2 to 134 of Table 21 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 21 R<sup>5</sup> is 1-methoxyethyl instead of methyl.

#### Table 22

Table 22 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is 1-methoxyethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 22 is the same as compound 1 of Table 2 except that in compound 1 of Table 22 R<sup>5</sup> is 1-methoxyethyl instead of methyl. Similarly, compounds 2 to 134 of Table 22 are the same as compounds 2 to 134 of Table 2, respectively, except that in the compounds of Table 22 R<sup>5</sup> is 1-methoxyethyl instead of methyl.

#### Table 23

Table 23 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-propyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, and R<sup>5</sup> is 1-methoxyethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 23 is the same as compound 1 of Table 3 except that in compound 1 of Table 23 R<sup>5</sup> is 1-methoxyethyl instead of methyl. Similarly, compounds 2 to 134 of Table 23 are the same as compounds 2 to 134 of Table

3, respectively, except that in the compounds of Table 23 R<sup>5</sup> is 1-methoxyethyl instead of methyl.

#### Table 24

Table 24 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is *n*-butyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is 1-methoxyethyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 24 is the same as compound 1 of Table 4 except that in compound 1 of Table 24 R<sup>5</sup> is 1-methoxyethyl instead of methyl. Similarly, compounds 2 to 134 of Table 24 are the same as compounds 2 to 134 of Table 4, respectively, except that in the compounds of Table 24 R<sup>5</sup> is 1-methoxyethyl instead of methyl.

#### Table 25

Table 25 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is ethyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is 3-cyanopropyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 25 is the same as compound 1 of Table 1 except that in compound 1 of Table 25 R<sup>5</sup> is 3-cyanopropyl instead of methyl. Similarly, compounds 2 to 134 of Table 25 are the same as compounds 2 to 134 of Table 1, respectively, except that in the compounds of Table 25 R<sup>5</sup> is 3-cyanopropyl instead of methyl.

#### Table 26

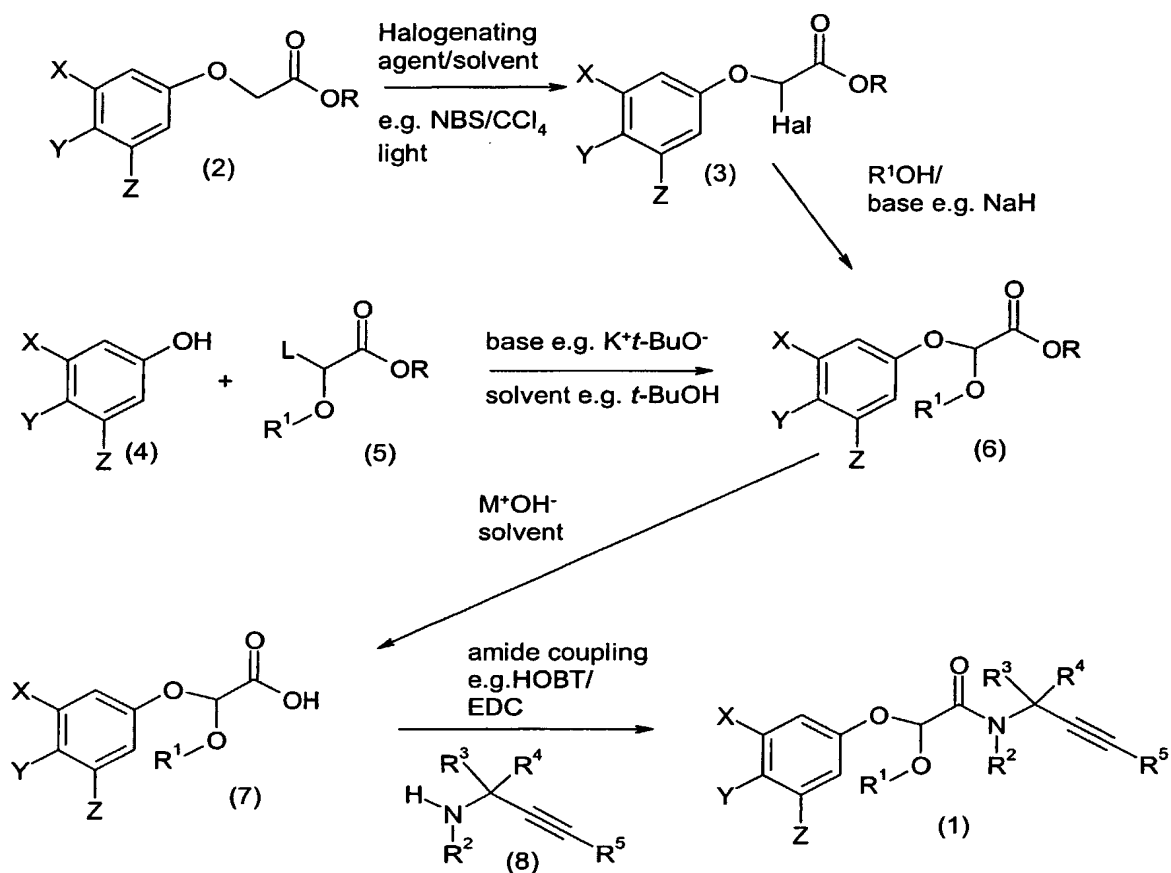
Table 26 consists of 134 compounds of the general formula (1), where R<sup>1</sup> is methyl, R<sup>2</sup> is hydrogen, R<sup>3</sup> and R<sup>4</sup> are both methyl, R<sup>5</sup> is 3-cyanopropyl and X, Y and Z have the values listed in Table 1. Thus compound 1 of Table 26 is the same as compound 1 of Table 2 except that in compound 1 of Table 26 R<sup>5</sup> is 3-cyanopropyl instead of methyl. Similarly, compounds 2 to 134 of Table 26 are the same as compounds 2 to 134 of Table 2, respectively, except that in the compounds of Table 26 R<sup>5</sup> is 3-cyanopropyl instead of methyl.

The compounds of general formula (I) may be prepared as outlined in Schemes 1 to 3 below, in which X, Y, Z, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> have the meanings given above, L is a leaving group such as halo, methylsulphonyloxy or arylsulphonyloxy (e.g. phenylsulphonyloxy), R is H or C<sub>1-4</sub> alkyl, as indicated, R<sup>a</sup> is H or C<sub>1-3</sub> alkyl, R<sup>b</sup> is H or C<sub>1-3</sub> alkyl, provided that when R<sup>a</sup> and R<sup>b</sup> are both alkyl their total number of carbon atoms



does not exceed 3,  $R^c$  is  $C_{1-6}$  alkyl, optionally substituted benzyl or optionally substituted thienylmethyl, DMF is *N,N*-dimethylformamide and DMAP is 4-dimethylaminopyridine. Compounds of general formula (1) may be prepared as shown in Scheme 1. Esters of formula (2), where R is  $C_{1-4}$  alkyl, may be halogenated to give haloesters of formula (3),  
5 where Hal is a halogen atom such as chlorine or bromine, by treatment with a suitable halogenating agent, such as *N*-bromosuccinimide, in a suitable solvent such as carbon tetrachloride, at between room temperature and the reflux temperature of the solvent. Haloesters of formula (3) can be reacted in  $R^1OH$  as solvent in the presence of a base such as calcium or potassium carbonate, or a metal alkoxide  $M^+R^1O^-$ , where M can be  
10 suitably sodium or potassium, at between 0°C and 40°C, preferably at room temperature, to give esters of formula (6). Alternatively esters of formula (6) can be formed by reaction of phenols of formula (4) and compounds of formula (5), in the presence of a base such as potassium *t*-butoxide, in suitable solvent such as *t*-butanol. The esters of formula (6) can be hydrolysed to acids of formula (7) by treatment with an alkali metal  
15 hydroxide, such as sodium hydroxide, in an aqueous alcohol ROH, at between room temperature and reflux. The acids of formula (7) can be condensed with the amines of formula (8) to give the compounds of general formula (1), using suitable activating reagents such as HOBT (1-hydroxybenzotriazole) and EDC (1-ethyl-3-*N,N*-dimethyl-aminopropylcarbodiimide hydrochloride).

Scheme 1



As shown in Scheme 2, amines of general formula (8), wherein R<sup>2</sup> is H, correspond to amines of general formula (12) and may be prepared by alkylation of a

5 silyl-protected aminoalkyne of general formula (10) using a suitable base such as *n*-butyl lithium and reacting with a suitable alkylating reagent R<sup>5</sup>L, such as an alkyl iodide, for example, methyl iodide, to form an alkylated compound of general formula (11). In a similar procedure, a silyl-protected aminoalkyne of general formula (10) may be reacted with a carbonyl derivative R<sup>a</sup>COR<sup>b</sup>, for example formaldehyde or acetaldehyde, using a

10 suitable base, such as *n*-butyl lithium, to provide an aminoalkyne (11) in which R<sup>5</sup> is a hydroxyalkyl moiety. The silyl protecting group may then be removed from a compound of general formula (11) with, for example, an aqueous acid to form an aminoalkyne of general formula (12). Aminoalkynes of general formula (12) may be further derivatised, for instance when R<sup>5</sup> is a hydroxyalkyl group, for example, by reacting a compound of

15 general formula (12) with a silylating agent, for example *tert*-butyldimethylsilyl chloride, to give a trialkylsilyloxy derivative of general formula (13). In another method, a

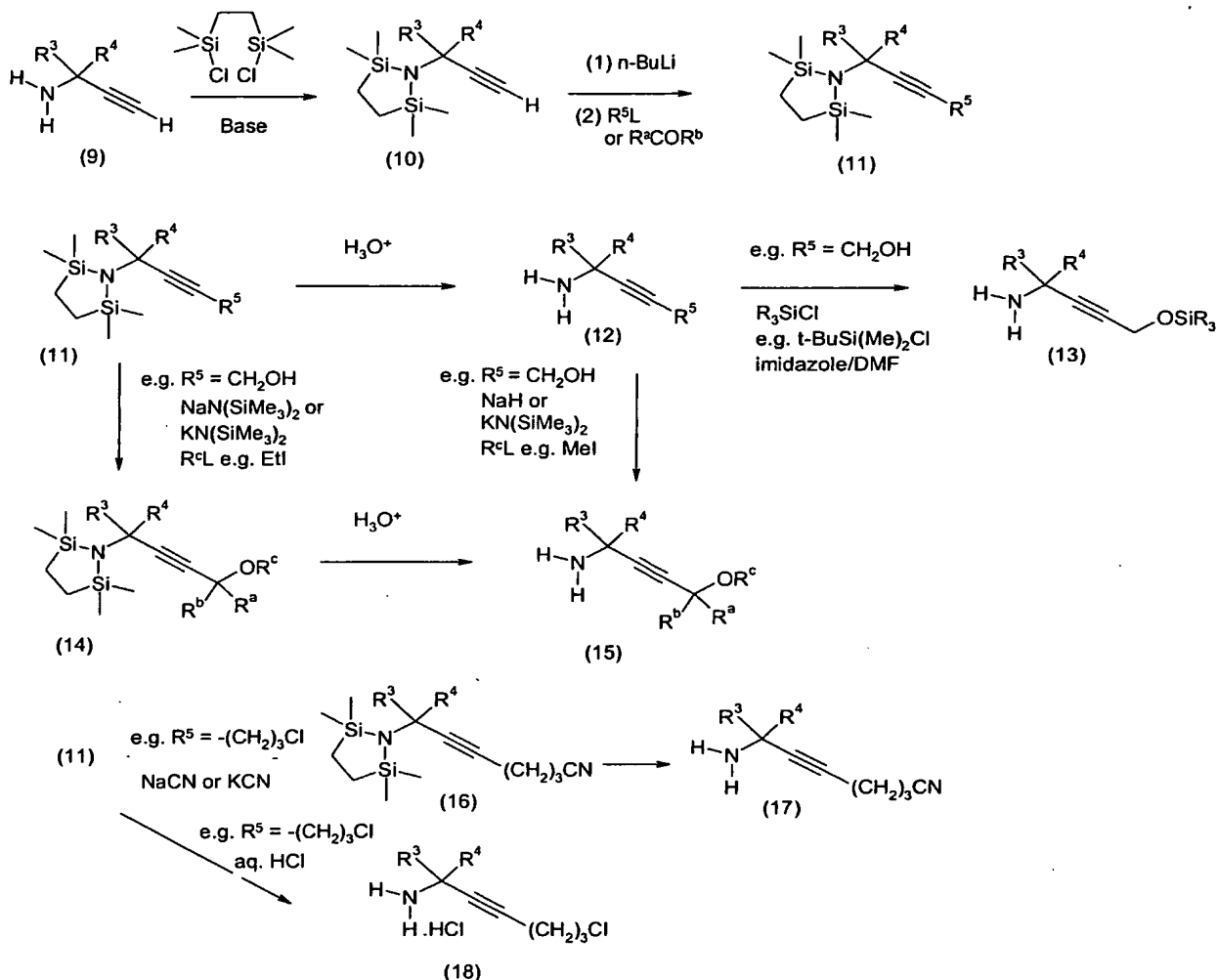
compound of general formula (12) may be treated with a base, such as sodium hydride or potassium *bis*(trimethylsilyl)amide, followed by a compound  $R^cL$ , where L represents a halogen or sulphonate ester such as  $OSO_2Me$ , or  $OSO_2$ -4-tolyl, to give compounds of general formula (15). In an alternative sequence, a compound of general formula (11)  
5 may be treated with a base, such as sodium or potassium *bis*(trimethylsilyl)amide, followed by a compound  $R^cL$ , where L represents a halogen or sulphonate ester such as  $OSO_2Me$ , or  $OSO_2$ -4-tolyl to give, after removal of the silyl protecting group, compounds of general formula (15).

Compounds of general formula (11), where  $R^5$  is for example 3-chloropropyl, can  
10 be reacted with a metal cyanide salt, such as sodium cyanide, to give compounds of general formula (16), which can then be hydrolysed, with for example an aqueous acid, to give the amines of general formula (17). Compounds of general formula (11), where  $R^5$  is for example 3-chloropropyl, can be hydrolysed, with for example an aqueous acid, to give amines of general formula (18).

15 The  $R^2$  group may be introduced into an aminoalkyne of general formula (12) by known techniques to form an amine of general formula (8), where  $R^2$  is other than H. Silyl-protected aminoalkynes of general formula (10) may be obtained by reacting amines of general formula (9) with 1,2-*bis*-(chlorodimethylsilyl)ethane in the presence of a suitable base, such as a tertiary organic amine base, for example, triethylamine.

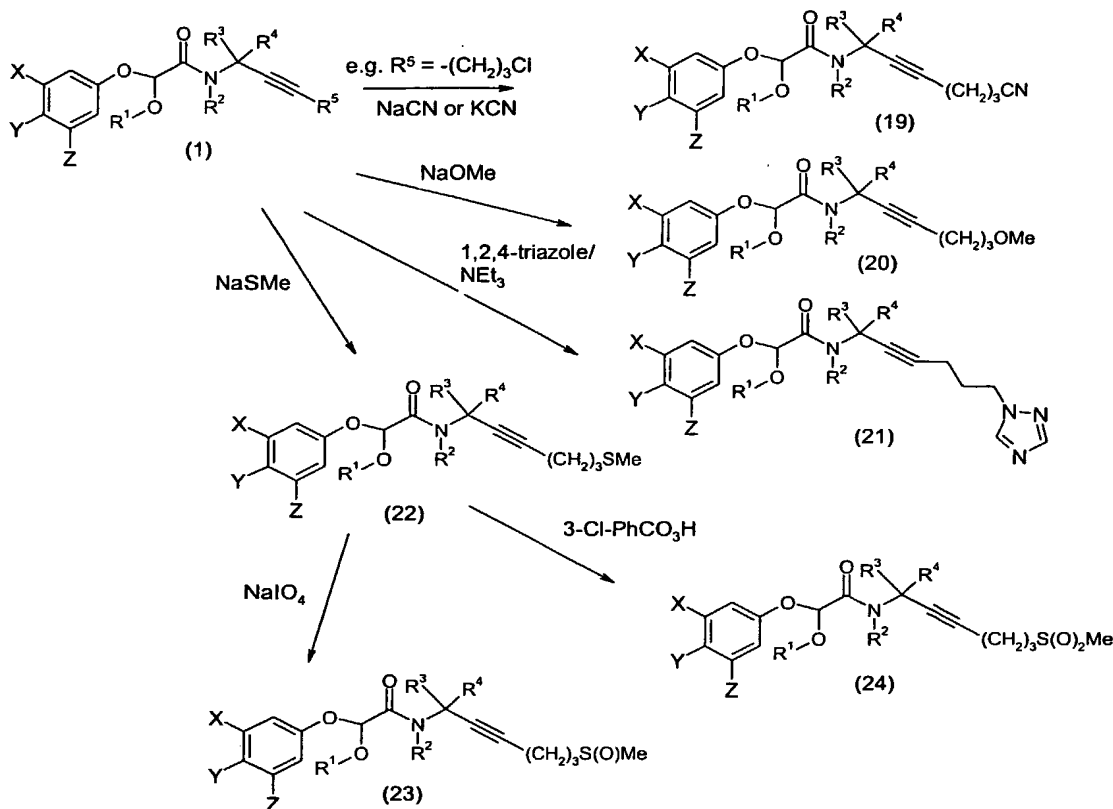
20 The amine (9) is either commercially available or may be prepared by standard literature methods (see, for example, EP-A-0834498) from commercially available materials.

Scheme 2



As shown in Scheme 3, compounds of general formula (1), where  $\text{R}^5$  is for example 3-chloropropyl can be reacted with various nucleophiles such as a metal cyanide salt, for example sodium cyanide, to give compounds of general formula (19), with metal alkoxides for example sodium methoxide, to give compounds of general formula (20), with 1,2,4-triazole in the presence of base such as triethylamine to give compounds of general formula (21), and with metal thioalkoxides, for example sodium methanethiolate to give compounds of general formula (22). Compounds of general formula (22) can be treated with oxidising agents such as sodium periodate, to give sulfoxides of general formula (23), or with oxidising agents such as *m*-chloroperbenzoic acid, to give sulphones of general formula (24)

Scheme 3



The compounds of formula (1) are active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia triticina* (or *recondita*), *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and

*Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts  
5 and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts;  
10 *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or  
15 frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts,  
20 *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts  
25 such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon,  
30 pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa

causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*,  
5 *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seeditiosum*) or lumber, notably *Cephalosporium fragrans*, *Ceratocystis* spp.,  
10 *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergii* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

15 The compounds of formula (1) show particularly good activity against the Oomycete class of pathogens such as *Phytophthora infestans*, *Plasmopara* species, e.g. *Plasmopara viticola* and *Pythium* species e.g. *Pythium ultimum*.

A compound of formula (1) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (1) may  
20 be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of formula (1), or a composition containing a compound of formula (1), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant  
25 growth medium, e.g. nutrient solution.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicator and antispore treatments.

The compounds of formula (1) are preferably used for agricultural, horticultural  
30 and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (1) to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other growth medium, a compound of formula

(1) is usually formulated into a composition which includes, in addition to the compound of formula (1), a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals that are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (1). The composition is generally used for the control of fungi such that a compound of formula (1) is applied at a rate of from 0.1g to 10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (1) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides a fungicidal composition comprising a fungicidally effective amount of a compound of formula (1) and a suitable carrier or diluent therefor.

In a still further aspect the invention provides a method of combating and controlling fungi at a locus, which comprises treating the fungi, or the locus of the fungi with a fungicidally effective amount of a composition comprising a compound of formula (1).

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (1).



Dustable powders (DP) may be prepared by mixing a compound of formula (1) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of formula (1) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (1) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (1) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (1) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgitic clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (1) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (1) in water or an organic solvent, such as a ketone, alcohol or glycol ether.

These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (1) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone), alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), *N*-alkylpyrrolidones (such as *N*-methylpyrrolidone or *N*-octylpyrrolidone), dimethyl amides of fatty acids (such as C<sub>8</sub>-C<sub>10</sub> fatty acid dimethylamide) and chlorinated hydrocarbons. An EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (1) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents that have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (1) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (1). SCs may be

prepared by ball or bead milling the solid compound of formula (1) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle.

- 5 Alternatively, a compound of formula (1) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of formula (1) and a suitable propellant (for example *n*-butane). A compound of formula (1) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (1) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

- 15 Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (1) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial
- 20 polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of formula (1) and they may be used for seed treatment. A compound of formula (1) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

- A composition may include one or more additives to improve the biological
- 25 performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (1)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which
- 30 may aid or modify the action of a compound of formula (1)).

A compound of formula (1) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a

water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC compositions described above.

- 5 Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

- 10 Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

- Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-  
15 *isopropyl*- and *tri-isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and  
20 tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

- Suitable SFAs of the non-ionic type include condensation products of alkylene  
25 oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple  
30 esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (1) may be applied by any of the known means of  
5 applying fungicidal compounds. For example, it may be applied, formulated or  
unformulated, to any part of the plant, including the foliage, stems, branches or roots, to  
the seed before it is planted or to other media in which plants are growing or are to be  
planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic  
culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied  
10 as a cream or paste formulation, applied as a vapour or applied through distribution or  
incorporation of a composition (such as a granular composition or a composition packed  
in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (1) may also be injected into plants or sprayed onto  
vegetation using electrodynamic spraying techniques or other low volume methods, or  
15 applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions)  
are generally supplied in the form of a concentrate containing a high proportion of the  
active ingredient, the concentrate being added to water before use. These concentrates,  
which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often  
20 required to withstand storage for prolonged periods and, after such storage, to be capable  
of addition to water to form aqueous preparations which remain homogeneous for a  
sufficient time to enable them to be applied by conventional spray equipment. Such  
aqueous preparations may contain varying amounts of a compound of formula (1) (for  
example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be  
25 used.

A compound of formula (1) may be used in mixtures with fertilisers (for example  
nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types  
include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the  
compound of formula (1).

30 The invention therefore also provides a fertiliser composition comprising a  
fertiliser and a compound of formula (1).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematocidal or acaricidal activity.

5 By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (1) alone. Further the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (1).

The compound of formula (1) may be the sole active ingredient of the  
10 composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the  
15 compound of formula (1); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of fungicidal compounds which may be included in the composition of the invention are AC 382042 (*N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy)  
20 propionamide), acibenzolar-S-methyl, alanycarb, aldimorph, anilazine, azaconazole, azafenidin, azoxystrobin, benalaxyl, benomyl, benthiavalicarb, biloxazol, bitertanol, blasticidin S, boscalid (new name for nicobifen), bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA 41396, CGA 41397, chinomethionate, chlorbenzthiazole, chlorothalonil, chlorozolate,  
25 clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cyamidazosulfamid, cyazofamid (IKF-916), cyflufenamid, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclocymet, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl  
30 thiophosphate, dimefluazole, dimetconazole, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethyl

(*Z*)-*N*-benzyl-*N*[(methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)- $\beta$ -alaninate, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil (AC 382042), fenciclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover,

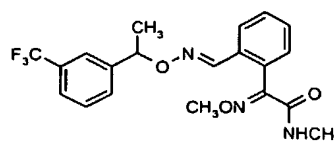
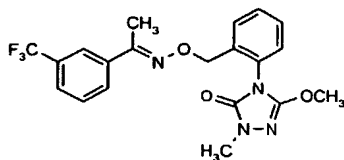
5 flumorph, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054,

10 LY211795, LY 248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metalaxyl M, metconazole, metiram, metiram-zinc, metominostrobin, metrafenone, MON65500 (*N*-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide), myclobutanil, NTN0301, neoasozin, nickel dimethyldithiocarbamate, nitrothale-isopropyl, nuarimol, ofurace, organomercury compounds, orysastrobin,

15 oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosphorus acids, phthalide, picoxystrobin, polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, proquinazid, prothioconazole, pyraclostrobin, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin,

20 quaternary ammonium compounds, quinomethionate, quinoxifen, quintozone, silthiofam (MON 65500), S-imazalil, simeconazole, sipconazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, 2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, tiadinil, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol,

25 triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb, ziram, zoxamide and compounds of the formulae:



The compounds of formula (1) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Some mixtures may comprise active ingredients, which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following Examples in which the following abbreviations are used:

ml = millilitres  
g = grammes  
ppm = parts per million  
M<sup>+</sup> = mass ion  
s = singlet  
d = doublet  
bs = broad singlet  
t = triplet

DMSO = dimethylsulphoxide  
DMF = *N, N*-dimethylformamide  
NMR = nuclear magnetic resonance  
HPLC = high performance liquid chromatography  
q = quartet  
m = multiplet  
ppm = parts per million

15

#### EXAMPLE 1

This Example illustrates the preparation of 2-(3,5-dichlorophenoxy)-2-(methoxy)-*N*-(2-methylpent-3-yn-2-yl) acetamide (Compound No. 4, Table 2 )

##### Step 1

To a solution of 2-(3,5-dichlorophenoxy)acetic acid (0.50g) in dichloromethane (12 ml) at 0°C was added 2 drops of DMF followed by oxalyl chloride (0.278ml) dropwise. The solution was stirred at room temperature for 2 hours and then evaporated affording the acid chloride (0.66g) as a pale yellow residue that was used straight away in the next step. A solution of the freshly prepared acid chloride in dichloromethane (10ml) was added to a solution of *t*-butanol (1ml) in triethylamine (2ml) at 0°C. The resulting



solution was stirred at room temperature and stored for 18 hours. The solvent was evaporated under reduced pressure and water added. The aqueous phase was extracted with ethyl acetate, the organic phase was washed with water, followed by aqueous saturated ammonium chloride and brine, and then dried over magnesium sulphate. The solvent was evaporated to give a brown oil (0.563g), which was purified by flash column chromatography on silica gel (40-60) eluting with ethyl acetate:hexane (1:2), to give t-butyl 2-(3,5-dichlorophenoxy)acetate as a pale yellow oil (0.42g).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.49 (9H,s); 4.49 (1H,s); 6.80 (2H,s); 6.99 (1H,s).

#### Step 2

To a solution of the product from Step 1 (0.42g) in carbon tetrachloride (7ml) at room temperature was added N-bromosuccinimide (0.271g). The resulting yellow solution was heated to 60°C and irradiated using a high-pressure mercury lamp UVL (~30 W) for 3 hours. The reaction was cooled to 0°C, the succinimide filtered, and washed with further carbon tetrachloride. The solvent was evaporated to dryness affording of t-butyl 2-bromo-2-(3,5-dichlorophenoxy)acetate as a pale yellow solid (0.54g).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.56 (9H,s); 6.29 (1H,s); 7.08 (2H,s); 7.17 (1H,s).

#### Step 3

To a solution of the product from Step 2 (0.10g) in methanol (3ml) at room temperature was added sodium methoxide (0.038g). The resulting pale yellow solution was stirred for 3 hours. The solvent was evaporated, and then water and ethyl acetate were added. The aqueous phase was separated and re-extracted with ethyl acetate. The organic fractions were combined, dried over magnesium sulphate and evaporated, giving t-butyl 2-methoxy-2-(3,5-dichlorophenoxy)acetate as a pale yellow oil (0.048g), which was used directly in the next step.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.49 (9H,s); 3.50 (3H,s); 5.32 (1H,s); 7.01 (2H,s); 7.05 (1H,s).

#### Step 4

To a solution of the product from Step 3 (0.048g) in methanol (1 ml) at room temperature was added the solution of sodium hydroxide (0.0125g) in water (0.5ml). The resulting mixture was heated to reflux for 30 minutes and the solvent evaporated. Water and ethyl acetate were added, the aqueous phase separated, acidified with dilute hydrochloric acid and extracted with ethyl acetate. The organic phase was dried over

magnesium sulphate, and evaporated to give 2-methoxy-2-(3,5-dichlorophenoxy)acetic acid (0.045g) as a pale yellow oil, which was used directly in the next step without further purification.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 3.55 (3H,s); 5.51 (1H,s); 7.04 (2H,s); 7.09 (1H,s).

5 Step 5

Triethylamine (0.032ml) was added to a stirred solution of 4-amino-4-methylpent-2-yne hydrochloride (0.024g) in DMF (1 ml) giving a white suspension. 2-Methoxy-2-(3,5-dichlorophenoxy)acetic acid (0.045mg) was added followed by 1-hydroxybenzotriazole (0.025g) and *N*-(3-dimethylaminopropyl)-*N'*-ethyl carbodiimide hydrochloride (0.035g). The white suspension was stirred at room temperature for 3 hours, stored for 18 hours and water added. The aqueous phase was extracted with diethyl ether and the organic phase washed with water, saturated sodium bicarbonate and then brine, dried over magnesium sulphate and evaporated to give a pale yellow oil (0.040g). This was purified by flash column chromatography on silica gel (40-60) eluting with ethyl acetate:hexane (1:4) to give the title product as a colourless oil (0.024g).

15  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.63 (3H,s); 1.64 (3H,s); 1.82 (3H,s); 3.50 (3H,s); 5.22 (1H,s); 6.68 (1H,bs); 7.05 (3H,s).

Preparation of 4-amino-4-methylpent-2-yne hydrochloride (for use in Step 5)

Stage 1

20 3-Amino-3-methylbutyne (commercially available as 90% aqueous solution; 16.6g) was dissolved in dichloromethane (150ml), dried over sodium sulphate and filtered to give a solution containing the amine (14.9g). To the stirred solution of amine under an atmosphere of nitrogen at ambient temperature was added dry triethylamine (48.4ml), 1,2-bis-(chlorodimethylsilyl)ethane (38.98g) in dichloromethane (100ml) was then added dropwise, maintaining the reaction temperature at 15°C by cooling. The mixture was stirred for 3 hours and the colourless solid, which had formed during the reaction, was filtered from solution and the filtrate was evaporated under reduced pressure to give a paste. The paste was extracted into hexane and refiltered. The filtrate was evaporated under reduced pressure and the oil obtained was distilled to give 1-(1,1-dimethyl-2-propynyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, (21.5g), b.p. 30 41°C at 0.06 mm Hg pressure.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.16 (12H,s); 0.60 (4H,s); 1.48 (6H,s); 2.24 (1H,s).

### Stage 2

The product from Step 1 (13.0g) in dry tetrahydrofuran (140ml) was cooled to -70°C under an atmosphere of nitrogen with stirring and a solution of *n*-butyl lithium (23.1ml of 2.5M solution in hexanes) was added at -65 to -70°C during 5 minutes. The mixture was allowed to warm to -5°C and methyl iodide (3.93ml) was added dropwise over 10 minutes. The reaction mixture was allowed to warm to 10°C when an exothermic reaction occurred. The mixture was maintained at 20°C by cooling for 2 hours then evaporated under reduced pressure to a small volume. The residue was dissolved in hexane, filtered to remove the insoluble material and evaporated under reduced pressure to give 1-(1,1-dimethyl-2-butylnyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane as a yellow oil, (13.0g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.10 (12H,s); 0.56 (4H,s); 1.40 (6H,s); 1.72 (3H,s).

### Stage 3

The product from Step 2 (13.0g) was added slowly to aqueous hydrochloric acid (35ml, 4M) at 0°C with stirring. The emulsion formed was stirred for 0.5 hours then taken to pH14 with aqueous sodium hydroxide (4M) while maintaining the reaction mixture at 0°C by cooling in ice. The aqueous mixture was extracted into dichloromethane (three times) and the extracts combined, dried over sodium sulphate and filtered. The filtrate was made acidic by adding an excess of a saturated solution of hydrogen chloride in 1,4-dioxan. The mixture was concentrated under reduced pressure until a colourless precipitate was formed. Hexane was added to the suspension and the solid was filtered from solution. The solid was washed with dry diethyl ether and placed under vacuum to remove any residual solvents to give the required product as a colourless solid, (5.0g).

<sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO) δ ppm: 1.74 (6H,s); 1.82 (3H,s); 8.74 (3H,bs).

### EXAMPLE 2

This example illustrates the preparation of 2-(3,5-dichlorophenoxy)-2-(ethoxy)-*N*-(2-methylpent-3-yn-2-yl) acetamide (Compound No. 4 of Table 1)

#### Step 1

Potassium *t*-butoxide (1.38g) was dissolved in *t*-butyl alcohol (13 ml). The mixture was stirred for 15 minutes at room temperature and 3,5-dichlorophenol (2.0g) added, followed by ethyl 2-bromo-2-ethoxyacetate (2.6g). The reaction was exothermic

with separation of potassium bromide. The reaction was stirred for 8 hours and then poured into water (45ml) and extracted with chloroform (10ml). The organic phase was washed with water, dried over magnesium sulphate and evaporated to give a colourless oil which was purified by flash column chromatography on silica gel (40-60) eluting with  
5 using ethyl acetate/hexane to give ethyl 2-(3,5-dichlorophenoxy)-2-(ethoxy)acetate as a colourless oil (1.925g).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.26 (3H,t); 1.31 (3H,t); 3.73 (1H, m); 3.81 (1H,m); 4.30 (2H,q); 5.48 (1H,s); 7.00 (2H,s); 7.06 (1H,s).

### Step 2

10 To the product from Step 1 (1.8g) in methanol (30 ml) at room temperature was added a solution of sodium hydroxide (0.49g) in water (10ml). The resulting mixture was heated to reflux for 15 minutes and the solvent evaporated, then water and ethyl acetate were added. The aqueous phase was separated, acidified with dilute hydrochloric acid and extracted with ethyl acetate. The organic phase was dried over magnesium sulphate  
15 and evaporated to give 2-(3,5-dichlorophenoxy)-2-(ethoxy)acetic acid (1.515g) as a white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm : 1.29 (3H,t); 3.75 (1H,m); 3.86 (1H,m); 5.54 (1H,s); 7.03 (2H,s); 7.09 (1H,s).

### Step 3

20 Triethylamine (0.264ml) was added to a stirred solution of 4-amino-4-methylpent-2-yne hydrochloride (0.253g) in DMF (7 ml) giving a white suspension. The product from Step 2 (0.5g) was added followed by 1-hydroxybenzotriazole (0.256g) and *N*-(3-dimethylaminopropyl)-*N'*-ethyl carbodiimide hydrochloride (0.363g). The white suspension was stirred at room temperature for 3 hours, stored for 18 hours, then water  
25 was added and the aqueous phase extracted with diethyl ether. The organic phase was washed with water, saturated sodium bicarbonate and then brine, dried over  $\text{MgSO}_4$ , and evaporated to give a white solid. This was recrystallised from hexane to give the title product as a white powder (0.324g), m.p. 76.5 °C.

30  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.29 (3H,t); 1.57 (3H,s); 1.64 (6H,s); 3.67 (1H,m); 3.84 (1H,m); 5.28 (1H,s); 6.68 (1H,bs); 7.06 (2H,s); 7.27 (1H,s).

## EXAMPLE 3

This example illustrates the preparation of 2-(3,5-dichlorophenoxy)-2-(ethoxy)-*N*-(1-*tert*-butyldimethylsilyloxy-4-methylpent-2-yn-4-yl) acetamide (Compound No. 4 of Table 17)

Step 1

5           1-(1,1-Dimethyl-2-propynyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (22.6g) in dry tetrahydrofuran (250ml) was cooled to -50°C under an atmosphere of nitrogen with stirring and a solution of *n*-butyl lithium ( 44ml, 2.5M solution in hexanes) was added dropwise over 10 minutes. The mixture was stirred for 0.5 hour, allowed to warm to -20°C then formaldehyde gas was bubbled through the mixture until no starting  
10           material remained as determined by glc analysis. On completion of reaction, the mixture was treated with water, the ether phase separated, the aqueous phase extracted with ethyl acetate (twice) and the organic extracts combined and washed with water (three times). The organic extract was dried over magnesium sulphate and evaporated under reduced pressure to give (1-hydroxy-4-methylpent-2-yn-4-yl)- 2,2,5,5-tetramethyl-1-aza-2,5-  
15           disilacyclopentane, (24.96g), as a pale yellow liquid.  
<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 0.00 (12H,s); 0.46 (4H,s); 1.32 (6H,s); 4.08 (2H,s); OH not observed.

Step 2

          The product from Step 1 (24.96g) was treated with dilute aqueous hydrochloric  
20           acid (300ml) and stirred at ambient temperature for 0.5 hour. The mixture was washed with diethyl ether (twice), the aqueous phase was evaporated under reduced pressure, distilled with toluene (twice) to remove residual water and the residual solid obtained was triturated with hexane to give 4-amino-1-hydroxy-4-methylpent-2-yne hydrochloride, (13.1g), as a cream coloured solid.

25           <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 1.48 (6H,s); 4.06 (2H,s); 5.32 (1H,s); 8.64 (3H,s).

Step 3

          4-Amino-1-hydroxy-4-methylpent-2-yne hydrochloride (4.40g) was dissolved in dry DMF (100ml) and triethylamine (4.44ml) was added. The suspension was stirred at ambient temperature for 10 minutes, imidazole (4.93g) was added followed by *tert*-butyl-  
30           dimethylsilyl chloride (5.24g) in dry DMF (40ml). The mixture was stirred at ambient temperature for 18 hours, diluted with water and extracted with diethyl ether (three times). The organic extracts were combined, washed with water (twice), dried over

magnesium sulphate and evaporated under reduced pressure to give 4-amino-1-*tert*-butyldimethylsilyloxy-4-methylpent-2-yne, (6.88g), as a yellow liquid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.04 (6H,s); 0.84 (9H,s); 1.30 (6H,s); 4.22 (2H,s).

#### Step 4

- 5        Triethylamine (0.119ml) was added to a stirred solution of the product from Step 3 (0.155g) in DMF (2 ml) giving a white suspension. Freshly prepared 2-ethoxy-2-(3,5-dichlorophenoxy)acetic acid (0.18g) was added in DMF (2 ml ) followed by *N*-hydroxy-benzotriazole (0.092g) and finally *N*-(3-dimethylaminopropyl)-*N'*-ethyl carbodiimide hydrochloride (0.131g). The white suspension was stirred at room temperature for 2
- 10       hours, and then stored for 2 days. Water was added and the aqueous phase was extracted with ethyl acetate. The organic phases were combined, washed with water and dried over magnesium sulphate, and evaporated to give yellow oil (0.317g). This was purified by flash column chromatography on silica gel (40-60) eluting with ethyl acetate:hexane (1:4), to give the title product as colourless oil (0.138g).
- 15        $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 0.12 (6H,s); 0.91 (9H,s); 1.28 (3H,t); 1.65 (3H,s); 1.67 (3H,s); 3.66 (1H,m); 3.83 (1H,m); 4.33 (2H,s); 5.27 (1H,s); 6.69 (1H,bs); 7.04 (3H,m).

#### EXAMPLE 4

This example illustrates the preparation of 2-(3,5-dichlorophenoxy)-2-(ethoxy)-*N*-(1-hydroxy-4-methylpent-2-yn-4-yl) acetamide (Compound No. 4 of Table 9).

- 20        To a solution of 2-(3,5-dichlorophenoxy)-2-(ethoxy)-*N*-(1-*tert*-butyldimethylsilyloxy-4-methylpent-2-yn-4-yl) acetamide (0.095g) in THF (2 ml) was added tetrabutylammonium fluoride (0.402ml of a 1.0 M solution in THF) dropwise over 5 minutes at 0°C. The mixture was stirred at room temperature for 2 hours, the solvent was evaporated and the residue was extracted with ethyl acetate. The ethyl acetate solution
- 25       was washed with ammonium chloride solution and brine, dried over magnesium sulphate, and evaporated to give a colourless oil (0.095g). This was purified by flash column chromatography on silica gel (40-60) eluting with ethyl acetate:hexane (1:1) to give the title compound as colourless oil (0.056g).
- 30        $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 1.28 (3H,t); 1.65 (6H,s); 3.67 (1H,m); 3.84 (1H,m); 4.27 (2H,s); 5.29 (1H,s); 6.70 (1H,bs); 7.05 (3H,m).

Table 21

Compound No.	Table No.	(Solvent): <sup>1</sup> H NMR chemical shifts in ppm from TMS, or melting point (mpt) or refractive index ( $n_D^{30}$ )
4	1	(CDCl <sub>3</sub> ): 1.28 (t,3H), 1.63 (s,3H), 1.64 (s,3H), 1.82 (s,3H), 3.67 (m,1H), 3.84 (m,1H), 5.28 (s,1H), 6.68 (bs,1H), 7.06 (m,3H)
4	2	(CDCl <sub>3</sub> ): 1.63 (s,3H), 1.64 (s,3H), 1.82 (s,3H), 3.50 (s, 3H), 5.22 (s,1H), 6.68 (bs,1H), 7.05 (s,3H)
4	5	Mpt. 67-70°C
2	6	Mpt. 76-80°C
4	6	$n_D^{30} = 1.5291$
8	6	$n_D^{30} = 1.5254$
4	9	(CDCl <sub>3</sub> ): 1.28 (t,3H), 1.65 (s,6H), 3.67 (m,1H), 3.84 (m,1H), 4.27 (s,2H), 5.29 (s,1H), 6.70 (bs,1H), 7.05 (m,3H)
4	13	(CDCl <sub>3</sub> ): 1.28 (t,3H), 1.67 (s,6H), 3.37 (s,3H), 3.67 (m,1H), 3.84 (m,1H), 4.11 (s,2H), 5.29 (s,1H), 6.68 (bs,1H), 7.04 (m,3H)
4	17	(CDCl <sub>3</sub> ): 0.12 (s,6H), 0.91 (s,9H), 1.28 (t,3H), 1.65 (s,3H), 1.67 (s,3H), 3.66 (m,1H), 3.83 (m,1H), 4.33 (s,2H), 5.27 (s,1H), 6.69 (bs,1H), 7.04 (m,3H).

## EXAMPLE 5

- 5 This Example illustrates the fungicidal properties of compounds of formula (1).

The compounds were tested in a leaf disk assay, with methods described below. The test compounds were dissolved in DMSO and diluted into water to 200 ppm. In the case of the test on *Pythium ultimum*, they were dissolved in DMSO and diluted into water to 20 ppm.

- 10 *Erysiphe graminis f.sp. hordei* (barley powdery mildew): Barley leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Erysiphe graminis f.sp. tritici* (wheat powdery mildew): Wheat leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Puccinia recondita f.sp. tritici* (wheat brown rust): Wheat leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed nine days after inoculation as preventive fungicidal activity.

*Septoria nodorum* (wheat glume blotch): Wheat leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Pyrenophora teres* (barley net blotch): Barley leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Pyricularia oryzae* (rice blast): Rice leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Botrytis cinerea* (grey mould): Bean leaf disks were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

*Phytophthora infestans* (late blight of potato on tomato): Tomato leaf disks were placed on water agar in a 24-well plate and sprayed with a solution of the test compound. After



allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

5 *Plasmopara viticola* (downy mildew of grapevine): Grapevine leaf disks were placed on agar in a 24-well plate and sprayed a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed seven days after inoculation as preventive fungicidal activity.

10 *Pythium ultimum* (Damping off): Mycelial fragments of the fungus, prepared from a fresh liquid culture, were mixed into potato dextrose broth. A solution of the test compound in dimethyl sulphoxide was diluted with water to 20ppm then placed into a 96-well microtiter plate and the nutrient broth containing the fungal spores was added. The test plate was incubated at 24°C and the inhibition of growth was determined photometrically after 48 hours.

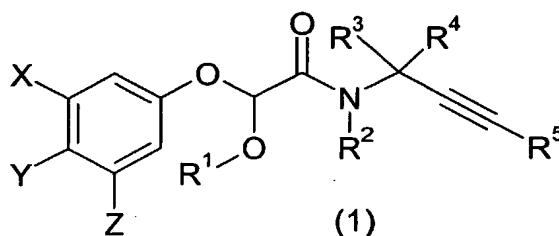
15 The following compounds gave greater than 60% control of disease (number of compound first, followed by table number in brackets):

*Plasmopara viticola*, compounds 4 (1), 4 (2), 4 (5), 2 (6), 4 (6), 4 (9), 4 (13), 4 (17);  
*Phytophthora infestans*, compounds 4 (1), 4 (2), 4 (5), 4 (9), 4 (17); *Erysiphe graminis f.sp. hordei*, compounds 4 (5), 2 (6); *Erysiphe graminis f.sp. tritici*, compound 4 (9), 4 (13), 4 (17); *Septoria nodorum*, compound 8 (6), 4 (13); *Pyricularia oryzae*, compound 2 (6); *Pyrenophora teres*, compound 8 (6); *Pythium ultimum*, compounds 4 (1), 4 (2), 4 (5), 2 (6), 4 (6), 8 (6), 4 (9), 4 (13).

20

## CLAIMS

1. The use as a plant fungicide of a compound of the general formula (1):



5 wherein

X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro, -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro, cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R'', -COR', -NR'COR'' or -NR'COOR''' where R' and R'' are independently H or C<sub>1-4</sub> alkyl and R''' is C<sub>1-4</sub> alkyl, provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group;

15 R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

20 R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

25 R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl, tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally

substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo,

hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub>

5 alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio,

halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl,

C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano,

thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -

CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup>

10 and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo-

(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or

benzyl, the phenyl and benzyl groups being optionally substituted with halogen,

C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

15 2. The use as a plant fungicide of a compound of the general formula (1) according to claim 1 wherein X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or methoxy and Y is H, chloro, bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and  
20 both Y and Z are H.

3. The use as a plant fungicide of a compound of the general formula (1) according to claim 1 or 2 wherein R<sup>1</sup> is methyl, ethyl, *n*-propyl, or *n*-butyl.

25 4. The use as a plant fungicide of a compound of the general formula (1) according to claim 1 or 2 wherein R<sup>1</sup> is methyl or ethyl.

5. The use as a plant fungicide of a compound of the general formula (1) according to any one of the preceding claims wherein R<sup>2</sup> is H.

30

6. The use as a plant fungicide of a compound of the general formula (1) according to any one of the preceding claims wherein both R<sup>3</sup> and R<sup>4</sup> are methyl.

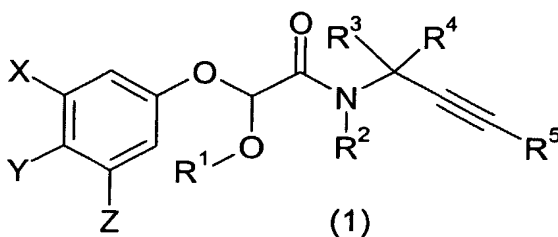
7. The use as a plant fungicide of a compound of the general formula (1) according to any one of the preceding claims wherein R<sup>5</sup> is H, methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxymethyl, 3-  
5 cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthiopropyl, 3-methanesulphinypropyl or 3-methanesulphonylpropyl.
8. The use as a plant fungicide of a compound of the general formula (1) according to claim 1 wherein  
10 X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro, -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro, cyano, nitro, C<sub>1-4</sub> alkoxy carbonyl, -CONR'R", -COR' or -NR'COR" where  
15 R' and R" are independently H or C<sub>1-4</sub> alkyl, provided that at least one of X and Z is other than H;  
R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group;  
R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;  
20 R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or  
R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and  
25 optionally substituted with halo or C<sub>1-4</sub> alkyl; and  
R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, C<sub>1-6</sub> alkylthio, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy or mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted  
30 thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or  
R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally

substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the  $R^5$  values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto,  $C_{1-4}$  alkyl,  $C_{2-4}$  alkenyl,  $C_{2-4}$  alkynyl,  $C_{1-4}$  alkoxy,  $C_{2-4}$  alkenyloxy,  $C_{2-4}$  alkynyloxy, halo( $C_{1-4}$ )alkyl, halo( $C_{1-4}$ )alkoxy,  $C_{1-4}$  alkylthio, halo( $C_{1-4}$ )alkylthio, hydroxy( $C_{1-4}$ )alkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl,  $C_{3-6}$  cycloalkyl,  $C_{3-6}$  cycloalkyl( $C_{1-4}$ )alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro,  $-NR^mR^n$ ,  $-NHCOR^m$ ,  $-NHCONR^mR^n$ ,  $-CONR^mR^n$ ,  $-SO_2R^m$ ,  $-OSO_2R^m$ ,  $-COR^m$ ,  $-CR^m=NR^n$  or  $-N=CR^mR^n$ , in which  $R^m$  and  $R^n$  are independently hydrogen,  $C_{1-4}$  alkyl, halo( $C_{1-4}$ )alkyl,  $C_{1-4}$  alkoxy, halo( $C_{1-4}$ )alkoxy,  $C_{1-4}$  alkylthio,  $C_{3-6}$  cycloalkyl,  $C_{3-6}$  cycloalkyl( $C_{1-4}$ )alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen,  $C_{1-4}$  alkyl or  $C_{1-4}$  alkoxy.

9. The use as a plant fungicide of a compound of the general formula (1) according to claim 1 wherein X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or methoxy and Y is H, chloro, bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and both Y and Z are H;  $R^1$  is methyl, ethyl, *n*-propyl or *n*-butyl;  $R^2$  is H;  $R^3$  and  $R^4$  are both methyl; and  $R^5$  is H, methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxymethyl, 3-cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthiopropyl, 3-methanesulphinylpropyl or 3-methanesulphonylpropyl.

10. A compound of the general formula (1):



wherein

X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro, -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro, cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R", -COR', -NR'COR" or -NR'COOR'" where R' and R" are independently H or C<sub>1-4</sub> alkyl and R'" is C<sub>1-4</sub> alkyl, provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group;

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl, tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

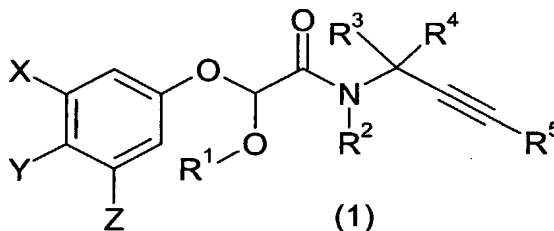
R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are

independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy;

- 5 provided that R<sup>5</sup> is not H when (i) X, Z, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and Y, and R<sup>2</sup> are both H, (ii) X, Z, R<sup>3</sup> and R<sup>4</sup> are all methyl, Y is chloro, R<sup>1</sup> is ethyl and R<sup>2</sup> is H, (iii) X and Z are both chloro, R<sup>1</sup> is methyl or ethyl, R<sup>3</sup> and R<sup>4</sup> are both methyl and Y and R<sup>2</sup> are both H, (iv) X, Y and Z are all chloro, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and R<sup>2</sup> is H, and (v) Y is chloro, Z is trifluoromethyl, R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are all methyl and X and R<sup>2</sup> are both H.
- 10

11. A compound of the general formula (1):



wherein

- 15 X, Y and Z are independently H, fluoro, bromo, iodo, C<sub>2-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy, halo-(C<sub>1-4</sub>)alkoxy, -S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro, -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro, cyano, nitro, C<sub>1-4</sub> alkoxycarbonyl, -CONR'R'', -COR', -NR'COR'' or -NR'COOR''' where R' and R'' are independently H or C<sub>1-4</sub> alkyl and R''' is C<sub>1-4</sub> alkyl, provided that at least one of X and Z is other than H; R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group;
- 20 R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;
- 25 R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4

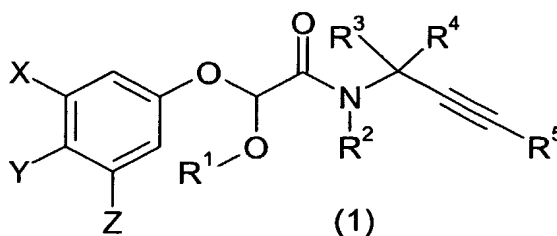
membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is H, C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)-alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or

R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo, hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)-alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

12. A compound of the general formula (1):



wherein

X, Y and Z are independently H, halogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>2-4</sub> alkenyl, halo(C<sub>2-4</sub>)alkenyl, C<sub>2-4</sub> alkynyl, halo(C<sub>2-4</sub>)alkynyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy,



-S(O)<sub>n</sub>(C<sub>1-4</sub>)alkyl where n is 0, 1 or 2 and the alkyl group is optionally substituted with fluoro, -OSO<sub>2</sub>(C<sub>1-4</sub>)alkyl where the alkyl group is optionally substituted with fluoro, cyano, nitro, C<sub>1-4</sub> alkoxy, carbonyl, -CONR'R'', -COR', -NR'COR'' or -NR'COOR''' where R' and R'' are independently H or C<sub>1-4</sub> alkyl and R''' is C<sub>1-4</sub> alkyl, provided that at least one of X and Z is other than H;

R<sup>1</sup> is a straight-chain C<sub>1-4</sub> alkyl group;

R<sup>2</sup> is H, C<sub>1-4</sub> alkyl, C<sub>1-4</sub> alkoxymethyl or benzyloxymethyl in which the phenyl ring of the benzyl moiety is optionally substituted with C<sub>1-4</sub> alkoxy;

R<sup>3</sup> and R<sup>4</sup> are independently H, C<sub>1-3</sub> alkyl, C<sub>2-3</sub> alkenyl or C<sub>2-3</sub> alkynyl provided that both are not H and that when both are other than H their combined total of carbon atoms does not exceed 4, or

R<sup>3</sup> and R<sup>4</sup> join with the carbon atom to which they are attached to form a 3 or 4 membered carbocyclic ring optionally containing one O, S or N atom and optionally substituted with halo or C<sub>1-4</sub> alkyl; and

R<sup>5</sup> is C<sub>1-4</sub> alkyl or C<sub>3-6</sub> cycloalkyl in which the alkyl or cycloalkyl group is optionally substituted with halo, hydroxy, C<sub>1-6</sub> alkoxy, cyano, C<sub>1-4</sub> alkylcarbonyloxy, aminocarbonyloxy, mono- or di(C<sub>1-4</sub>)alkylaminocarbonyloxy, -S(O)<sub>n</sub>(C<sub>1-6</sub>)alkyl where n is 0, 1 or 2, triazolyl (e.g. 1,2,4-triazol-1-yl), tri(C<sub>1-4</sub>)-alkylsilyloxy, optionally substituted phenoxy, optionally substituted thienyloxy, optionally substituted benzyloxy or optionally substituted thienylmethoxy, or R<sup>5</sup> is optionally substituted phenyl, optionally substituted thienyl or optionally substituted benzyl,

in which the optionally substituted phenyl and thienyl rings of the R<sup>5</sup> values are optionally substituted with one, two or three substituents selected from halo,

hydroxy, mercapto, C<sub>1-4</sub> alkyl, C<sub>2-4</sub> alkenyl, C<sub>2-4</sub> alkynyl, C<sub>1-4</sub> alkoxy, C<sub>2-4</sub> alkenyloxy, C<sub>2-4</sub> alkynyloxy, halo(C<sub>1-4</sub>)alkyl, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, halo(C<sub>1-4</sub>)alkylthio, hydroxy(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy(C<sub>1-4</sub>)alkyl, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR<sup>m</sup>R<sup>n</sup>, -NHCOR<sup>m</sup>, -NHCONR<sup>m</sup>R<sup>n</sup>, -CONR<sup>m</sup>R<sup>n</sup>, -SO<sub>2</sub>R<sup>m</sup>, -OSO<sub>2</sub>R<sup>m</sup>, -COR<sup>m</sup>, -CR<sup>m</sup>=NR<sup>n</sup> or -N=CR<sup>m</sup>R<sup>n</sup>, in which R<sup>m</sup> and R<sup>n</sup> are independently hydrogen, C<sub>1-4</sub> alkyl, halo(C<sub>1-4</sub>)alkyl, C<sub>1-4</sub> alkoxy, halo(C<sub>1-4</sub>)alkoxy, C<sub>1-4</sub> alkylthio, C<sub>3-6</sub> cycloalkyl, C<sub>3-6</sub> cycloalkyl(C<sub>1-4</sub>)alkyl, phenyl or benzyl, the

phenyl and benzyl groups being optionally substituted with halogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy.

13. A compound according to claim 10 or 12 wherein X, Y and Z are all chloro or methyl, or X and Z are both chloro or bromo and Y is H or methyl, or X and Z are both methyl or methoxy and Y is H, chloro, bromo or alkylthio, or X is methoxy, Y is H and Z is cyano or chloro, or X is methyl, Y is H and Z is ethyl, or X is chloro, bromo or trifluoromethyl and both Y and Z are H; R<sup>1</sup> is methyl, ethyl, *n*-propyl or *n*-butyl; R<sup>2</sup> is H; R<sup>3</sup> and R<sup>4</sup> are both methyl; and R<sup>5</sup> is methyl, hydroxymethyl, methoxymethyl, 1-methoxyethyl, *tert*-butyldimethylsilyloxy-methyl, 3-cyanopropyl, 3-(1,2,4-triazol-1-yl)propyl, 3-methylthiopropyl, 3-methanesulphinylpropyl or 3-methanesulphonylpropyl.
14. A process for preparing a compound of the general formula (1) as defined in claim 1 as herein described.
15. A fungicidal composition comprising a fungicidally effective amount of a compound of the general formula (1) as defined in claim 1 and a suitable carrier or diluent therefor.
16. A method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of the general formula (1) as defined in claim 1 or a composition according to claim 15 to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium.

# INTERNATIONAL SEARCH REPORT

PCT/GB 03/04612

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N39/04 C07C235/20 C07C235/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 001 721 A (STAUFFER CHEMICAL CO) 2 May 1979 (1979-05-02) cited in the application the whole document ---	1-16
X	US 4 062 977 A (BAKER DON R ET AL) 13 December 1977 (1977-12-13) cited in the application claim 1; table I ---	10, 14
X	US 4 049 423 A (BAKER DON R ET AL) 20 September 1977 (1977-09-20) cited in the application column 1 -column 2 -----	10, 11, 14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

15 January 2004

Date of mailing of the international search report

10/05/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Bertrand, F

# INTERNATIONAL SEARCH REPORT

PCT/GB 03/04612

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0001721	A	02-05-1979	US 4154849 A	15-05-1979
			US 4168319 A	18-09-1979
			AR 220917 A1	15-12-1980
			AU 522381 B2	03-06-1982
			AU 4103378 A	01-05-1980
			BR 7807046 A	08-05-1979
			CA 1117961 A1	09-02-1982
			CA 1122225 A2	20-04-1982
			CS 201020 B2	31-10-1980
			DD 144499 A5	22-10-1980
			DD 149890 A5	05-08-1981
			DE 2861093 D1	03-12-1981
			DK 477978 A	27-04-1979
			DK 522282 A	23-11-1982
			EG 13498 A	30-09-1982
			EP 0001721 A2	02-05-1979
			ES 474563 A1	16-12-1980
			GR 72949 A1	17-01-1984
			IL 55820 A	29-02-1984
			JP 54073743 A	13-06-1979
			NZ 188730 A	08-05-1980
			PH 13317 A	13-03-1980
			PT 68701 A ,B	01-11-1978
			RO 75384 A1	30-11-1980
			RO 81038 A1	01-02-1983
			RO 85275 A1	29-09-1984
			YU 250378 A1	30-04-1983
			ZA 7806007 A	31-10-1979
			CS 211398 B2	26-02-1982
			ES 480039 A1	01-04-1980
			IL 62884 A	30-04-1982
US 4062977	A	13-12-1977	NONE	
US 4049423	A	20-09-1977	US 4083867 A	11-04-1978